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Analytical Methods for Determination of POHC (Principal Organic Hazardous Constituents) in Combustion Products

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ANALYTICAL METHODS FOR DETERMINATION OF POHC IN COMBUSTION PRODUCTS

by

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16. ABSTRACT The paper gives an overview of generalized analytical procedures for determining designated principal organic hazardous constituents (POHCs) in combustion products; it also gives some examples of the techniques used for compounds such as 2,3,7,8-tetrachlorodibenzodioxin, selenourea, and several organo-arsenicals. Emissions from hazardous-waste combustion must be monitored to determine the destruction removal efficiency (DRE) for each designated POHC. Analytical methods for more than 150 POHCs have been reviewed. A generalized HRGC/LRMS method to determine volatile, thermally stable POHCs has been developed. A method based on HPLC with UV detection has also been developed to provide an alternative for determining nonvolatile or thermally labile compounds. The generalized methods are applicable to many compounds, but specific POHCs may require variations in GC/MS or HPLC procedures. Inclusion in the paper does not mean that the sampling or analysis method is an official EPA method. Official test methods for hazardous waste related programs are published in SW-846, Test Methods for Evaluating Solid Waste, as well as in the Federal Register.

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Toxicity	Principal Organic Hazardous Constituents	06T
Sampling		14B
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Abstract

The emissions from hazardous-waste combustion must be monitored to determine the Destruction Removal Efficiency (DRE) for each designated Principal Organic Hazardous Constituent (POHC). Analytical methodology for more than 150 POHCs has been reviewed. A generalized high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS) method to determine volatile, thermally stable POHCs has been developed. A method based on high performance liquid chromatography (HPLC) with ultraviolet (UV) detection has also been developed to provide an alternative for the determination of nonvolatile or thermally labile compounds. The generalized methods are applicable to many compounds, but specific POHCs may require variations in gas chromatography/mass spectrometry (GC/MS) or HPLC procedures. This paper will present an overview of the generalized procedures as well as some examples of the techniques used for compounds such as 2,3,7,8-tetrachlorodibenzodioxin, selenourea, and several organo-arsenicals.

This paper has been produced by EPA's Office of Research and Development as part of on-going studies in support of regulatory programs and of EPA's Office of Solid Waste, EPA Regional Offices, and appropriate state agencies. The document contains state-of-the-art analysis methods for determination of hazardous waste incinerator performance. This paper covers the laboratory phase of the study and does not include a discussion of actual combustion samples. It is intended as a reference work to be used by personnel of the regulatory groups, personnel associated with engineering R&D, and the regulated community.

Inclusion in this paper does not mean that the sampling or analysis method is an official EPA method. Official test methods for hazardous waste related programs are published in SW-846, "Test Methods for Evaluating Solid Waste" (1), as well as in the Federal Register.

INTRODUCTION

Background

As part of the Resource Conservation and Recovery Act (RCRA) (2), the U.S. Environmental Protection Agency (EPA) has promulgated proposed, interim, and final regulations for the owners and operators of facilities that treat hazardous wastes by incineration. The purpose of the regulations is to ensure that such incinerators are operated in an environmentally responsible manner. The Consolidated Permit Regulations (Parts 122-125, 40 CFR) (3) cover a range of activities, including operational performance standards, waste analysis, trial burns, monitoring and inspections, recordkeeping and reporting, and the establishment of emission-control criteria. The specific details for each incinerator facility are authorized by facility permits.

An important criterion upon which all operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. This value, which is defined in terms of waste-input levels and stack-output levels of the potentially hazardous substances, must be greater than 99.99% for proper incineration. A list of potential "principal organic hazardous constituents" (POHCs) is found in Appendix VIII, Part 261, 40 CFR (4). The list includes organic, organometallic, and inorganic compounds. Organic POHCs may be selected from this list.

The overall strategy for waste characterization includes test procedures to determine the characteristics of the waste and analysis procedures to determine the composition of the waste. The manual, "Sampling and Analysis Methods for Hazardous Waste Combustion" (5), includes test procedures for proximate, survey, and directed analysis. An overview of this analytical approach is shown in Figure 1 (5). Our brief discussion here is limited to directed analysis. Modification of analytical methods applicable to the identification and quantification of POHCs is now of primary interest to us.

The directed analysis portion of the waste-characterization scheme provides qualitative confirmation of compound identity and quantitative data for the potentially hazardous constituents that might reasonably be expected to be present in the waste, based on engineering judgment and on the results of proximate and survey analyses. Directed analysis does not involve the screening of every waste sample against the complete hazardous-component list. Directed analysis consists of the minimum set of analytical techniques that can be applied to the waste for qualitative identification and quantitative determination of the components that are actually present.

In practice, the results of the directed analysis will establish whether the waste contains the suspected pollutant and will establish the concentration range at which the pollutant may be expected to be found. Directed analysis will also be used to confirm and quantify any unexpected hazardous components not identified in the survey analysis. These data are essential for selection of the appropriate POHCs to be monitored and for the prediction of hazardous combustion by-products in stack effluents.

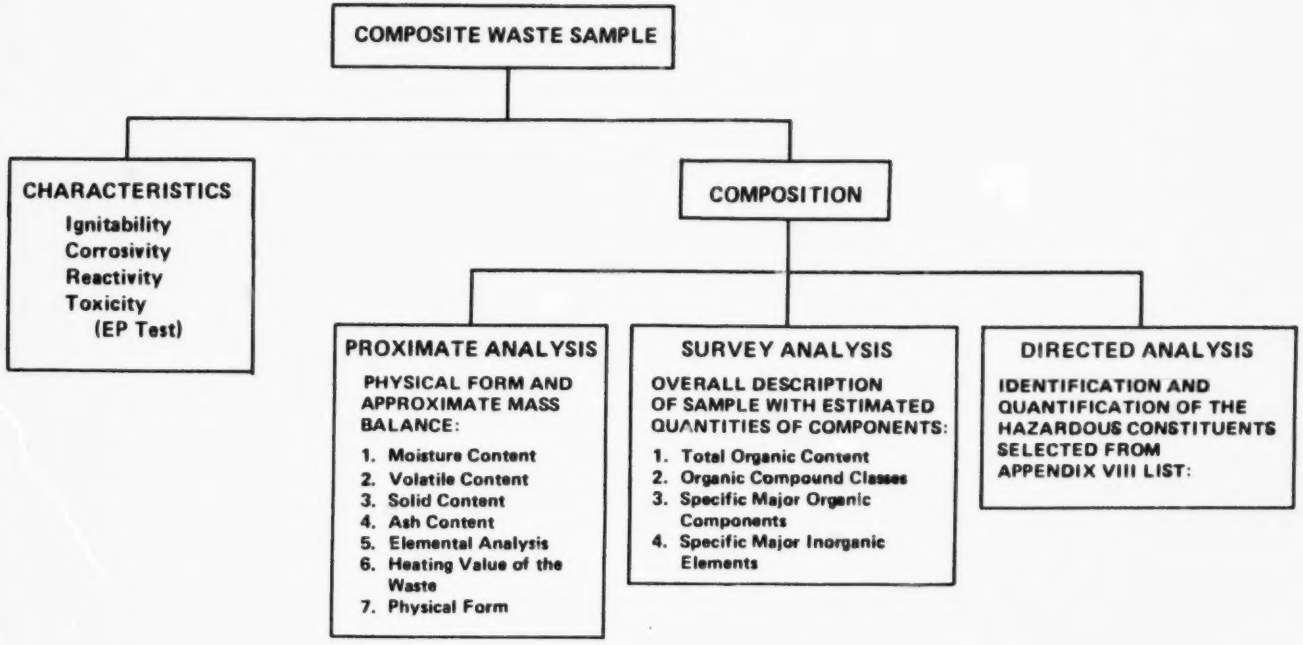

Figure 1. Overview of the analytical approach for waste characterization.

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Purpose

Approximtely 400 compounds are included in Appendix VIII, Part 261, 40 CFR. Previous work (6,7) involved the evaluation of generalized GC/flame ionization detection (FID), GC/MS, and HPLC/UV methods for the determination of approximately 150 compounds from this list of POHCs. However, the survey analysis portion of a waste-characterization scheme often targets specific compounds for determination in incinerator effluent that are not amenable to previously developed methods (6,7). Therefore, current research involves the development of specific GC/FID, GC/MS, and HPLC/UV methods for the determination of several of these compounds. This paper presents preliminary data on methodology for two groups of compounds, organometallics and chlorinated dibenzodioxins.

Organometallic compounds such as benzenearsonic acid(I), hydroxydimethylarsine oxide (cacodylic acid)(II), phenylmercuric acetate(III), selenourea(IV), and tetraethyl lead(V) were selected as candidate POHCs for this study. Tetraethyl lead was easily measured by the generalized GC/FID and GC/MS procedures. Selenourea required a new HPLC/UV option. The two organoarsenic compounds and the organomercury compound could not be determined by HPLC/UV with adequate sensitivity and were not easily determined by GC. Volatile hydride generation has been demonstrated to be useful for the determination of inorganic and organic arsenic compounds (8). Soderquist et al. (9) has demonstrated that hydroiodic acid (HI) will convert hydroxydimethylarsine oxide to iododimethylarsine. We have demonstrated that iodide derivatives of compounds I, II, and III can be determined by GC/FID and GC/MS.

The determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in water, soils and sediment, and incinerators (10-14) has been of increasing interest. The U.S. EPA has developed methods for the determination of 2,3,7,8-TCDD in soils and sediment (15) and in municipal and industrial waste water (16). These methods use isomer-specific high-resolution (HR) capillary GC columns and selected-ion-monitoring (SIM) low-resolution (LR) MS. This paper compares the generalized GC/MS procedure developed in earlier work (6,7) with the more selective and sensitive procedures developed by the U.S. EPA.

EXPERIMENTAL

Materials

2,3,7,8-TCDD was obtained as a 7.97-µg/mL solution from the U.S. EPA. $^{13}C_{12}$-2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD were obtained from Cambridge Isotope Laboratories. Tetraethyl lead was obtained from Ethyl Corporation. Hydroiodic acid (Kodak) was a 55% (w/v) certified grade without stabilizer. Hydroxydimethylarsine oxide (cacodylic acid) was obtained from Chem Services, Inc. Selenourea, benzenearsonic acid, and phenylmercuric acetate were obtained from Aldrich Chemicals. All other chemicals were reagent grade or better.

Equipment

The GC/FID work was performed on a Hewlett-Packard Model 5840 GC. GC/MS work was performed on a Hewlett-Packard Model 5985A GC/MS. Both instruments were equipped for split-splitless injections on capillary columns.

The HPLC/UV work was performed on a Hewlett-Packard Model 1084B HPLC with a variable wavelength UV-VIS detector (190-600 nm) and an automatic sampling system.

Procedures

The generalized GC/MS, GC/FID conditions are listed below:

• Instruments:	HP5985A GC/MS; HP5840 GC/FID
• Columns:	Two matched SE-54 bonded-fused-silica capillary columns, 0.32-mm ID, 25-m length
• Carrier gas:	Helium, 30 cm/s (2 mL/min)
• Injection:	2 µL splitless
• Column temperature program:	40 to 280 °C at 10 °C/min, hold 15 min
• Injection temperature:	290 °C
• FID temperature:	300 °C
• MS parameters:	Scan 41 to 450 amu/s. Electron ionization at 70 eV. Source temperature set to 200 °C. Capillary column plumbed directly into the ion source.

The initial operating conditions chosen were a synthesis of conditions that would allow the separation and detection of as many compounds as possible. Modifications of temperatures and rates may be necessary or desirable to optimize the analysis for specific compounds.

The selected-ion-monitoring GC/MS conditions for 2,3,7,8-TCDD are listed below:

• Instrument:	HP5985A GC/MS
• Column:	Chrompack CP-SIL-88 fused-silica capillary, 0.22-mm ID, 60-m length
• Carrier gas:	Helium, 30 cm/s (2 mL/min)
• Injection:	3 µL splitless
• Column temperature program:	45 °C for 3 min, to 190 °C at 25 °C/min, to 240 °C at 5 °C/min, hold
• Injection temperature:	290 °C
• MS parameters:	Selected ions m/z 257, 320, 322, 328, 332, 334 for 70 ms each. Source temperature set to 200 °C. Capillary column plumbed directly into the ion source.

The HPLC/UV conditions are listed below:

• Instrument:	HP 1084B with a variable wavelength UV/VIS detector
• Column:	Waters µBondapak-CN, 10-µm particle size, 3.9-mm ID, 30-cm length
• Solvents:	A = 1% acetic acid in distilled deionized water B = acetonitrile
• Gradient program	10% B for 5 min, 10 to 100% B in 30 min, hold at 100% B for 5 min. Flow rate of 1 mL/min.

Sample Preparation: Sorbent Tubes

Sorbent tubes were prepared by packing 4 mm ID glass tubes with ≈7.5 cm (400 mg) of XAD-2 resin (Applied Science 100/120 mesh) and with silanized glass-wool plugs, front and back (Figure 2). These tubes were spiked (in triplicate) with aliquots of the organometallics in methanol. The first set of tubes was allowed to air dry for ≈1 hour before extracting with two 5-mL portions of methanol. The methanol extracts were combined in 50-mL centrifuge tubes and blown dry with a gentle stream of N_2. The residues were derivatized with 1-mL of HI, and the derivatized organometallics were extracted into 10 mL of hexane. A blank (unspiked) XAD-2 sorbent tube was carried through the procedure with the spiked tubes.

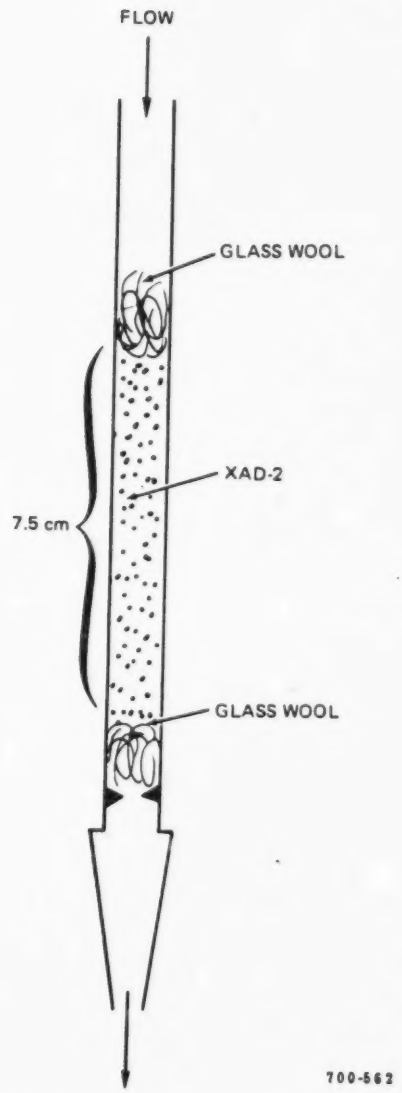


Figure 2. XAD-2 sorbent tube.

Another set of tubes was packed, spiked, and allowed to sit for 3 days. The tubes were then extracted, and the extract was derivatized and analyzed in the same manner as above.

The last set of sorbent tubes was packed, spiked, and then allowed to sit for 1 hour. Warm, moist air (~ 85% relative humidity) was then pulled through the tubes for 2 hours at a rate of ~ 200 mL/min. A flask was placed at the exit end of the sorbent tube to trap condensate. The condensate in the flask was also analyzed for the organometallics.

Filter Samples

Glass-fiber filters (Gelman) were spiked in triplicate with 1-mL aliquots of a methanol solution of the organometallics (~ 1 mg/mL). Filters were allowed to air-dry. Extraction of the filters with methanol was carried out in 200-mL screw-capped centrifuge bottles. The first triplicate set was extracted and analyzed the same day of spiking. Filters were extracted with two 10-mL portions of methanol shaking on a gyratory shaker for 10 min. The methanol extracts were dried with a gentle stream of N_2. The residues were derivatized with 1-mL of HI. The derivatized organometallics were extracted into 10 mL of hexane. A blank filter was carried through the procedure with the spiked filters. Another triplicate set of filters was spiked, allowed to sit for 3 days, and then analyzed in the same manner.

Water Samples

Deionized water (50 mL) was spiked with 1-mg quantities of the organometallics. A 1-mL aliquot of HI was added to one sample with shaking. The derivatized water sample was then extracted with 20 mL of hexane. Another spiked water sample (50 mL) was dried to a residue using a gentle stream of N_2. This residue was then derivatized with a 1-mL aliquot of HI. The derivatized organometallics were then extracted into 20 mL of hexane.

QUALITY CONTROL

The GC/FID, GC/MS, and HPLC/UV methods were calibrated with standard solutions of POHCs. For each POHC in the study, a four- or eight-point calibration curve was generated. For GC/FID and GC/MS determinations, relative responses were used to give calibration curves. Relative response was calculated as a ratio of detector responses for the standard POHC to that of the internal standard, anthracene-d_{10}. The HPLC/UV method was calibrated by an external standard technique. Internal standardization of the HPLC/UV method was not used because a single internal standard that was appropriate for all HPLC/UV analyses could not be selected. Based on the expected POHCs in a sample, the analyst will be able to select an internal standard that will not coelute with a POHC or with other organic compounds from the sample. Also, a linear-regression equation and correlation coefficient from the calibration data were calculated. Typically, correlation coefficients are in excess of 0.9900. The calibration curve can be used to estimate the sensitivity expected in the determination of a particular analyte. Also, each curve demonstrates

the linearity of the detector response within the range of quantities investigated.

The precision of the determinations by GC/FID and GC/MS was assessed by triplicate injections of a standard solution of each POHC. However, for HPLC/UV determinations, five replicate injections were made. The estimate of precision of the replicate determinations is expressed as the relative standard deviation (RSD). The range of RSD for GC/FID is 1 to 4%. The range of RSD for GC/MS is 2 to 9%. The RSD for HPLC/UV determinations is less than 5%.

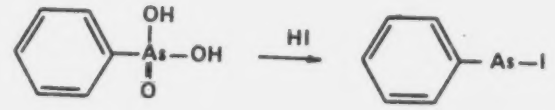
Any laboratory that participates in the analysis of POHCs will likely follow a formal quality control program. The relative retention times, on-column detection limits, chromatograms, calibration curves, ion relative abundances, mass spectra, and relative standard deviations in this paper will be a guide for other analytical laboratories. Because of subtle differences among laboratories and analytical instrumentation, laboratories should generate data that will establish formal criteria for the analysis of POHCs.

RESULTS AND DISCUSSION

Organometallics

The five organometallic compounds targeted required three different methods of analysis. The general GC/FID and GC/MS methods were used to determine tetraethyl lead(V). Benzenearsonic acid(I), hydroxydimethylarsine oxide(II), and phenylmercuric acetate(III) were derivatized with hydroiodic acid to improve thermal stability and volatility. Selenourea(IV) and benzenearsonic acid(I) were determined by HPLC/UV.

The hydroiodic acid derivatization procedure is similar to the procedure used by Soderquist et al. (9). Equations 1, 2, and 3 describe the derivatization process for the three organometallics.



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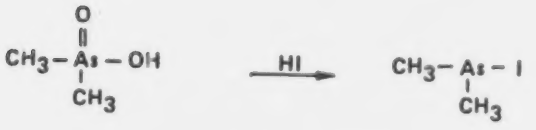

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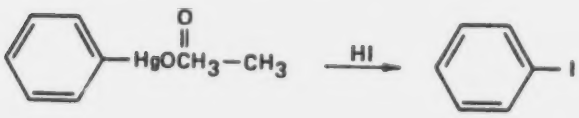

(3)

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The reactions appear to proceed rapidly and quantitatively.

The general GC/FID and GC/MS procedures were used to determine the derivatives.

In Table 1 we present the GC/FID and GC/MS relative retention times and estimated on-column detection limits for compounds I, II, III, V, and 2,3,7,8-TCDD. The on-column detection limit is the quantity of each analyte that was estimated to give a detector response of twice the background signal. Typical values ranged from 0.7 to 11.8 ng for GC/FID and from 0.8 to 8.8 ng for GC/MS. In Table 2 we list the five most abundant mass fragments of the compounds or compound derivatives reported in this study. The absolute intensity of the base peak in the mass spectrum was used to develop calibration curves. The precision of replicate determinations for GC/FID and GC/MS is presented in Table 3. Figure 3 is a representative chromatogram of a mixture of the HI derivatives of compounds I, II, and III. (Anthracene-d_{10} is the internal standard.) The GC/MS calibration curves for tetraethyl lead, benzenearsonic acid (HI derivative), hydroxydimethylarsine oxide (HI derivative), and phenylmercuric acetate (HI derivative) are presented in Figure 4. The mass spectra of the HI derivatives are presented in Figures 5a through 5c.

HPLC-UV

In Table 4 we present the retention times, on-column detection limits, and wavelengths of detection of the two POHCs determined by HPLC/UV. The high detection limit for benzenearsonic acid indicates that the HI derivatization method is the method of choice. Selenourea is easily determined by the HPLC/UV method presented in the experimental section.

Laboratory Recovery of Organometallics from Amberlite XAD-2 Resin, Glass-Fiber Filters, and Water

The sampling methods required for the ultimate analysis of POHCs in hazardous wastes and incinerator effluents during trial burns will vary according to the nature of the wastes. Prior to incineration, the hazardous waste may be a solid, liquid, slurry, or sludge. After incineration, the POHCs may be found in bottom ash, fly ash/electrostatic precipitator (ESP) catches, scrubber water, or stack gas.

Sampling of the effluent streams of a hazardous-waste incinerator serves several purposes. During trial burns, the measurement of POHCs in the stack-gas effluent is an integral part of the calculation of DRE values to determine if the incinerator meets its performance criteria. The sampling of stack-gas components is important to the hazardous-waste-incinerator permitting process. Some of the sampling methods available to collect volatile POHCs at low concentrations in stack gas are the Modified Method 5 (MM5) sampling train, the Source Assessment Sampling System (SASS), and the Volatile Organic Sampling Train (VOST). These systems use specific sorbents to collect POHCs. We selected XAD-2 resin, a general purpose sorbent for organic compounds to determine the recovery of POHCs from the sorbent. We also used glass-fiber

Table 1. Summary of GC/FID and GC/MS Determinations of Candidate POHCs

Compound	GC/FID		GC/MS	
	Relative retention time[a]	On-column detection limit,[b] ng	Relative retention time[a]	On-column detection limit,[b] ng
Benzenearsonic acid (I)	0.986	2.2	0.975	6.4
Hydroxydimethylarsine oxide (II)	0.324	11.8	0.301	5.7
Phenylmercuric acetate (III)	0.471	1.0	0.460	8.8
Tetraethyl lead (V)	0.570	0.7	0.568	1.5
2,3,7,8-TCDD	1.26	0.7	1.23	0.8[c]

[a]Relative to the retention time of anthracene-d_{10}.

[b]Quantity required to yield a detector response twice the magnitude of the background signal.

[c]The detection limit by single ion monitoring is 0.1 ng.

Table 2. Summary of Characteristic EI Ions and Relative Abundances of Candidate POHCs

Compound	Mol wt.	Characteristic EI Ions (relative abundance)				
		1	2	3	4	5
Benzenearsonic acid (I)	202[a]	279(100)	152(23)	151(12)	280 (8)	202 (6)
Hydroxydimethylarsine oxide (II)	138[b]	232(100)	217(62)	105(23)	89(15)	202(15)
Phenylmercuric acetate (III)	337[c]	204(100)	77(73)	51(32)	50(24)	127(17)
Tetraethyl lead (V)	324	237(100)	295(73)	235(50)	208(47)	236(45)
2,3,7,8-TCDD	320	322(100)	320(78)	324(48)	257(25)	259(21)

[a]Molecular weight of HI derivative = 279

[b]Molecular weight of HI derivative = 232

[c]Molecular weight of HI derivative = 204

Table 3. Precision of Response Factors[a] for GC/FID and GC/MS Determinations

Compound	GC/FID		GC/MS	
	Mean (n=3)	RSD%	Mean (n=3)	RSD%
Benzenearsonic acid (I)	0.345	2	0.131	3
Hydroxydimethylarsine oxide (II)	0.066	1	0.366	9
Phenylmercuric acetate (III)	0.142	1	0.160	4
Tetraethyl lead (V)	0.406	3	0.268	2
2,3,7,8-TCDD	0.041	4	0.046	3

[a]Response Factor = $\frac{\text{Area Std}}{\text{Area IS}} \cdot \frac{\text{Conc IS}}{\text{Conc Std}}$

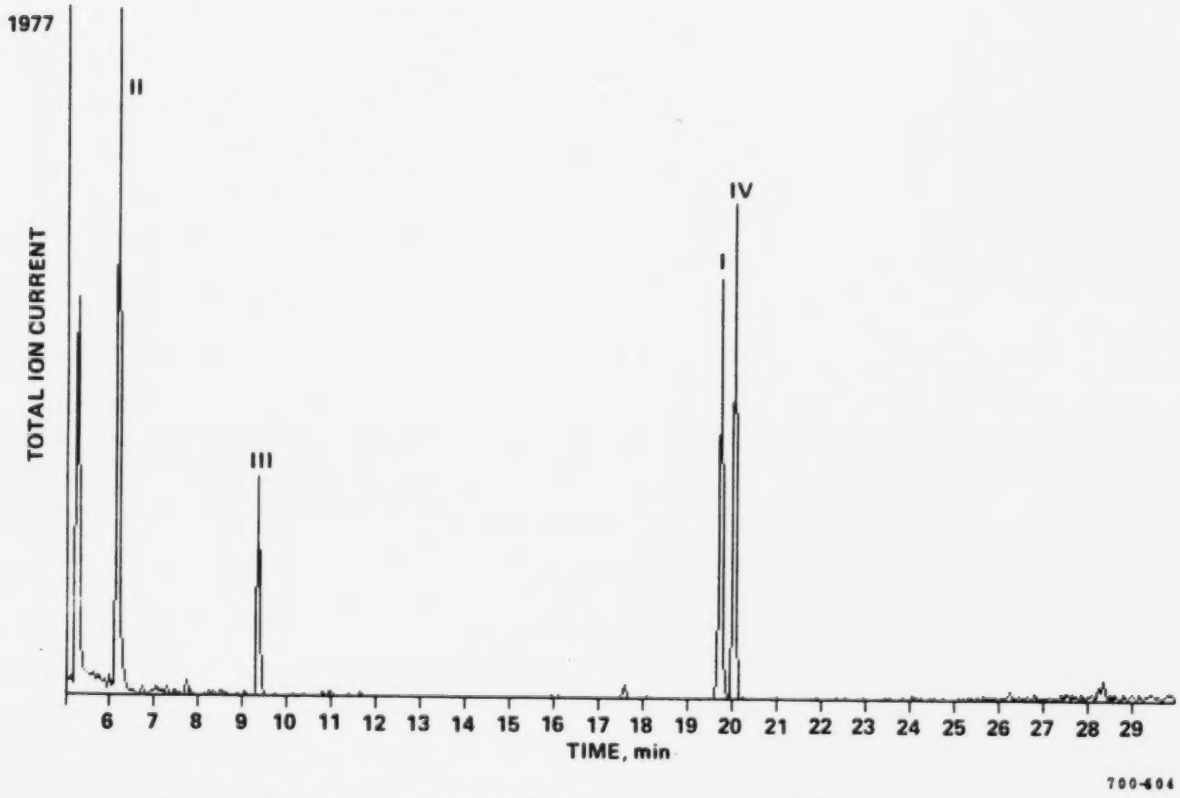

Figure 3. Total ion current GC/MS of the HI derivatives of benzenearsonic acid (I), hydroxydimethylarsine oxide (II), and phenylmercuric acetate (III). Anthracene-d_{10} is IV. Approximately 50 ng of each compound was injected.

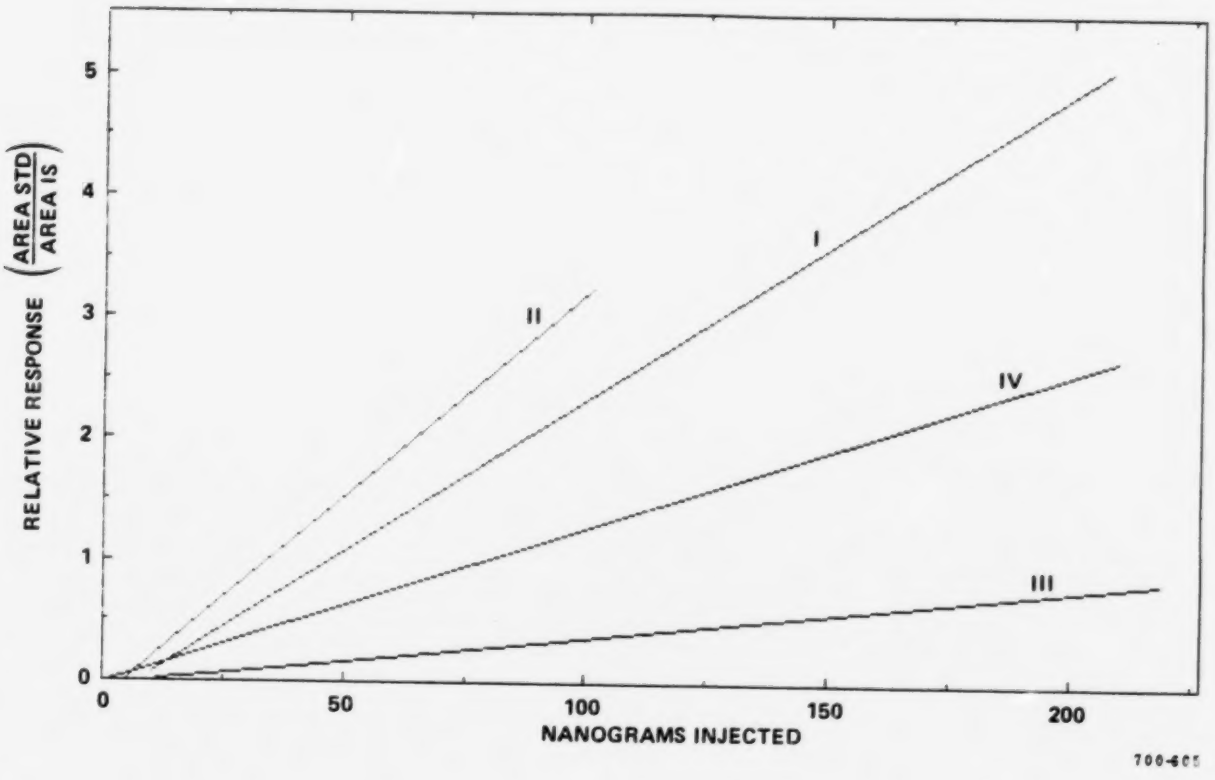

Figure 4. Calibration curves for the HI derivatives of benzenearsonic acid (I), hydroxydimethylarsine oxide (II), and phenylmercuric acetate (III). Tetraethyl lead is IV.

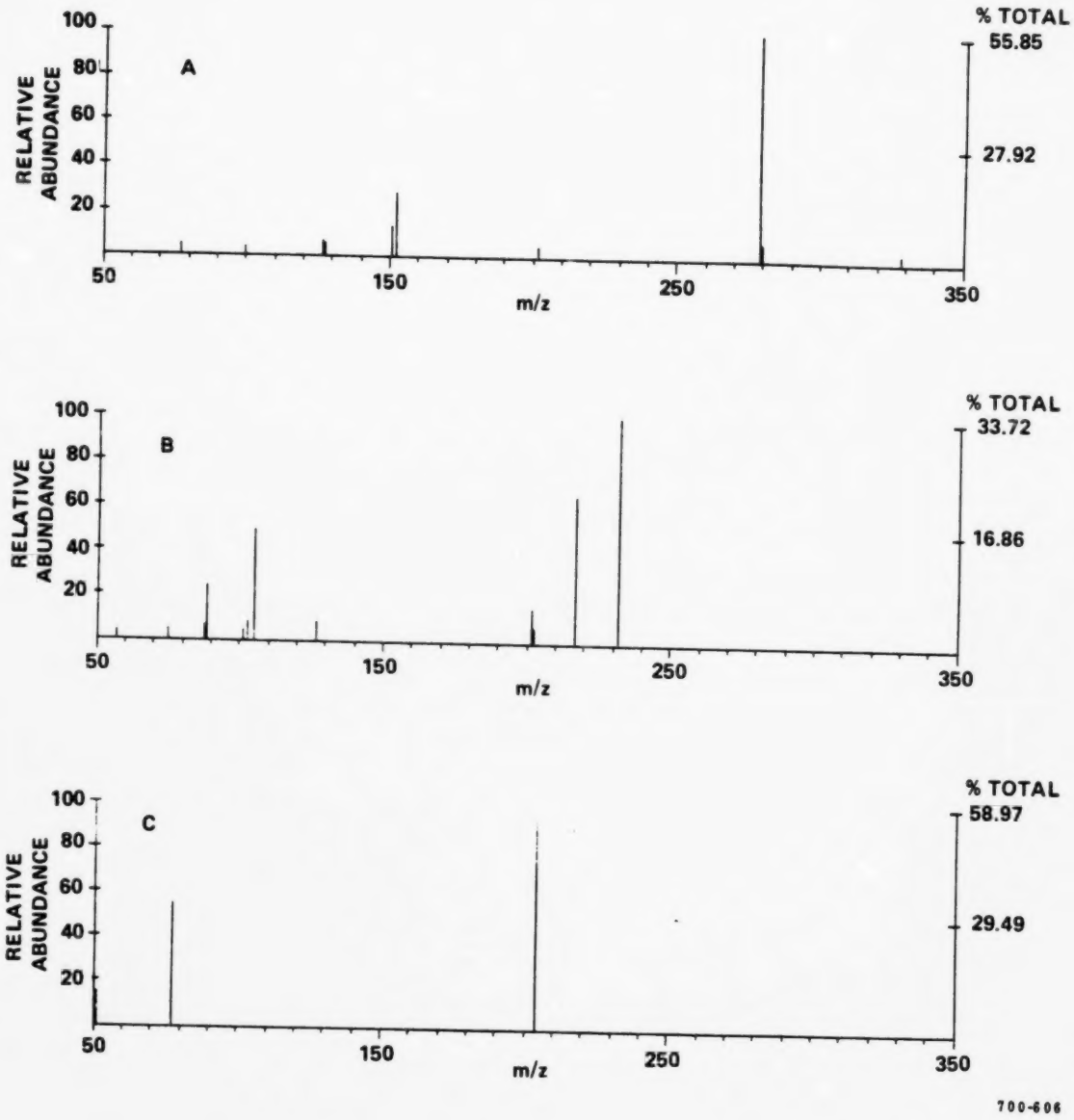

Figure 5. Mass spectra of HI derivatives of benzenearsonic acid (A), hydroxydimethylarsine oxide (B), and phenylmercuric acetate (C).

Table 4. Summary of HPLC/UV Determination of Candidate POHCs

Compound	Retention time, min	On-column detection limit[a], µg	Precision summary		
			Quantity injected, µg	Mean area counts x 10^{-3}	RSD, %
Selenourea[b]	3.5	0.0123	0.784	241	4.3
Benzenearsonic acid[c]	4.1	1.14	12.38	198	1.8

[a]Estimated quantity injected that is required to yield a response twice the magnitude of the background signal.

[b]Wavelength of detection = 254 nm.

[c]Wavelength of detection = 263 nm.

filters and distilled deionized water to examine recovery from other parts of the sampling system. Methanol was used to extract benzenearsonic acid, hydroxydimethylarsine oxide, and phenylmercuric acetate from the XAD-2 resins and glass-fiber filters. Water samples were evaporated to dryness prior to derivatization. Methylene chloride was used to extract tetraethyl lead. The determination of the analytes was performed by GC/FID or GC/MS. Figure 2 is a diagram of one of the XAD-2 tubes used. A representative GC/MS chromatogram of a standard containing HI derivatives of three organometallics is Figure 6a. Figure 6b is a GC/MS chromatogram of an extract of an XAD-2 tube that was exposed to moist air (~ 85% humidity) at a flow rate of 200 mL/min for 2 hours. The XAD-2/moist-air experiment was performed six times. One tube showed significant water condensation. The water was evaporated to dryness and the residue was derivatized; the sum of the amounts found in the condensate and the XAD-2 resin was comparable to the other five determinations. Additional XAD-2 tubes were spiked and extracted after approximately 1 hour and spiked and extracted after approximately 72 hours. Table 5 presents the recoveries of the three organometallics from the XAD-2 resin experiments. In a separate experiment, tetraethyl lead was spiked onto XAD-2 tubes, exposed to moist air and extracted with methylene chloride. Table 5 also presents the data from the tetraethyl lead tubes.

The three organometallics were also spiked onto glass-fiber filters, extracted with methanol, derivatized, and analyzed by GC/FID. The recovery data are presented in Table 6 for three spiked filters.

Because the three compounds were known to be somewhat water soluble, the compounds were spiked into 50 mL of distilled deionized water. Two experiments were performed. First, HI was added to the spiked water and the water was extracted with hexane, and then the extract was analyzed by GC/FID. Recoveries of hydroxydimethylarsine oxide and benzenearsonic acid were less than 3% and of phenylmercuric acid were greater than 100%. Second, the compounds were spiked into 50 mL of distilled deionized water, evaporated to dryness, derivatized, and dissolved in hexane, and the hexane was analyzed by GC/FID. The recovery of hydroxydimethylarsine oxide was 68%, of benzenearsonic acid was 87%, and of phenylmercuric acetate was 83%.

2,3,7,8-Tetrachlorodibenzo-p-dioxin

The determination of 2,3,7,8-TCDD by HRGC/LRMS was performed using partial-scan MS (m/z 41-450 in 1 s) and selected ion monitoring (SIM) (m/z 257, 320, 322, 328, 332, and 334). The fused-silica bonded-phase SE-54 column was compared with the 2,3,7,8-TCDD isomer-specific fused-silica CP-SIL-88 column. Figure 7a is the partial-scan mass and ion chromatogram obtained with the SE-54 column. The injected solution is a 5-ng/μL 2,3,7,8-TCDD standard (m/z 257, 320, 322) which also contained 12.5 ng/μL of d_{10}-anthracene (m/z 188), 0.2 ng/μL $^{37}Cl_4$-TCDD (m/z 328) and 0.5 ng/μL $^{13}C_{12}$ 2,3,7,8-TCDD (m/z 332, 334). Figure 7b is the chromatogram obtained with the CP-SIL-88 column. A 5-ng/μL 2,3,7,8-TCDD standard containing 0.2 ng/μL $^{37}Cl_4$-2,3,7,8-TCDD and 0.5 ng/μL $^{13}C_{12}$-2,3,7,8-TCDD was used. The peak obtained with the more polar CP-SIL-88 column is somewhat broader than the peak from the SE-54 column, but the more polar CP-SIL-88 GC column provides separation of the 2,3,7,8-TCDD isomer

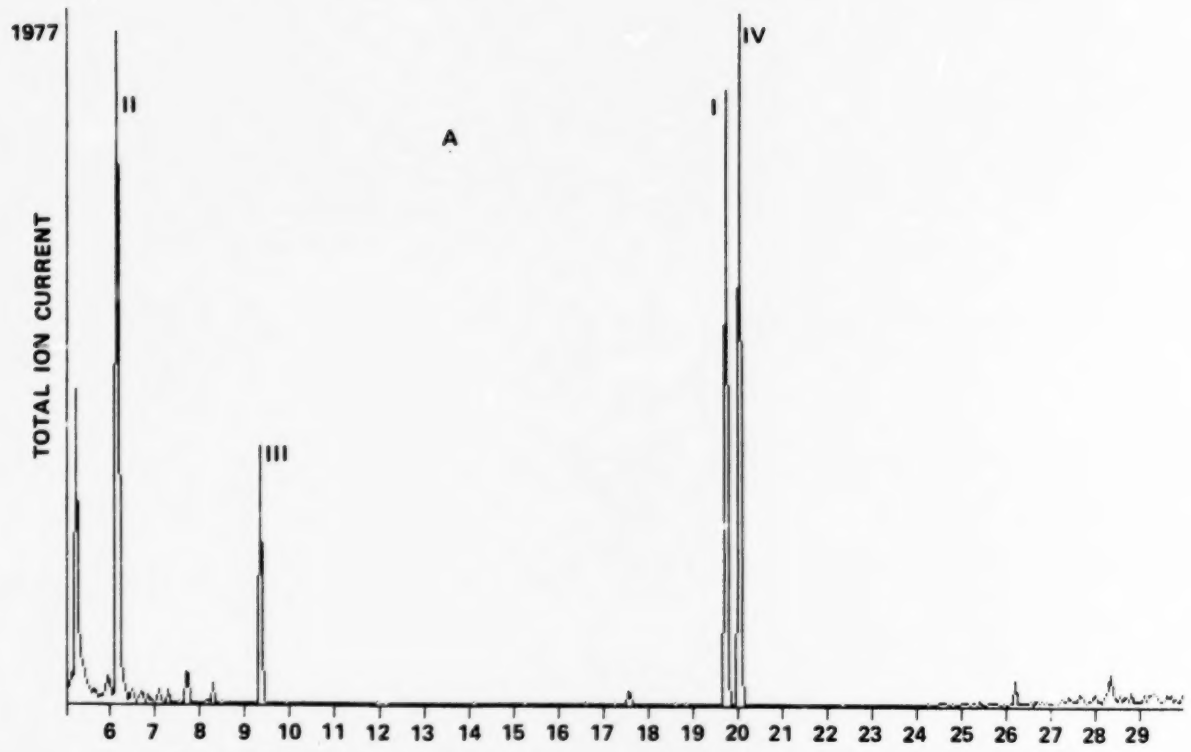

Figure 6A. GC/MS of standard containing the HI derivatives of benzenearsonic acid (I), hydroxydimethylarsine oxide (II), and phenylmercuric acetate (III). Anthracene-d_{10} is IV.

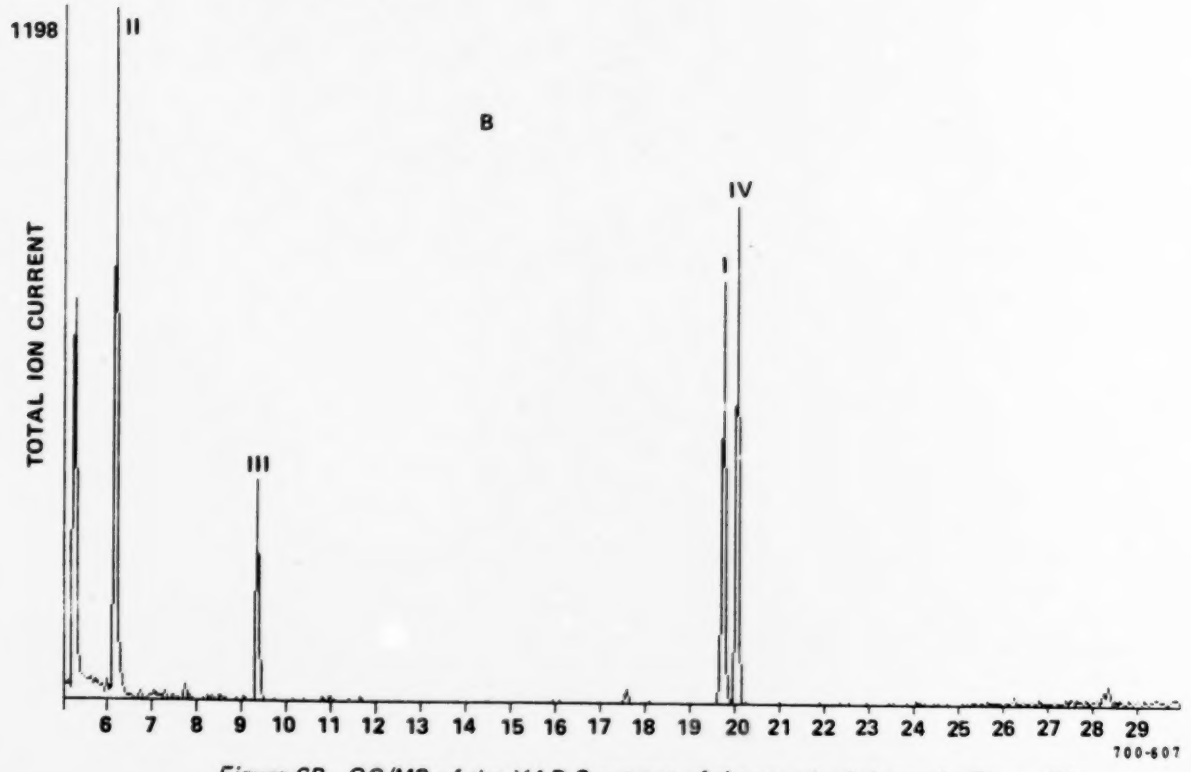

Figure 6B. GC/MS of the XAD-2 extract of the standard shown in Figure 6A.

Table 5. Recovery of POHCs from XAD-2 Resin

Compound	Extracted after 1 hour: Amount added, µg	Extracted after 1 hour: Avg % recovery (n=3)	Extracted after 1 hour: % RSD	Extracted after 72 hours: Amount added, µg	Extracted after 72 hours: Avg % recovery (n=3)	Extracted after 72 hours: % RSD	Extracted after moist-air exposure: Amount added, µg		Extracted after moist-air exposure: Avg % recovery (n=6)	Extracted after moist-air exposure: % RSD
Benzenearsonic acid (I)	252	100	2.4	292	84	7.0	245[a,b]	315[b]	104	10
Hydroxydimethylarsine oxide (II)	278	92	7.8	278	69	8.7	300[b]	318[b]	82	16
Phenylmercuric acetate (III)	222	54	6.3	222	65	3.1	252[b]	300[b]	76	8
Tetraethyl lead[c] (V)							248		91[d]	3

[a]One sample had significant water breakthrough. Combinations of the derivatives of the liquid and XAD-2 extracts were analyzed.

[b]Two sets of three samples were analyzed.

[c]Only the moist-air exposure experiment was performed.

[d]n=3.

Table 6. Recovery of POHCs from Glass-Fiber Filters After 72 Hours

Compound	Amount added, µg	Avg % recovery (n=3)	% RSD
Benzenearsonic acid (I)	252	114	3.2
Hydroxydimethylarsine oxide (II)	278	99	4.2
Phenylmercuric acetate (III)	222	97	4.6

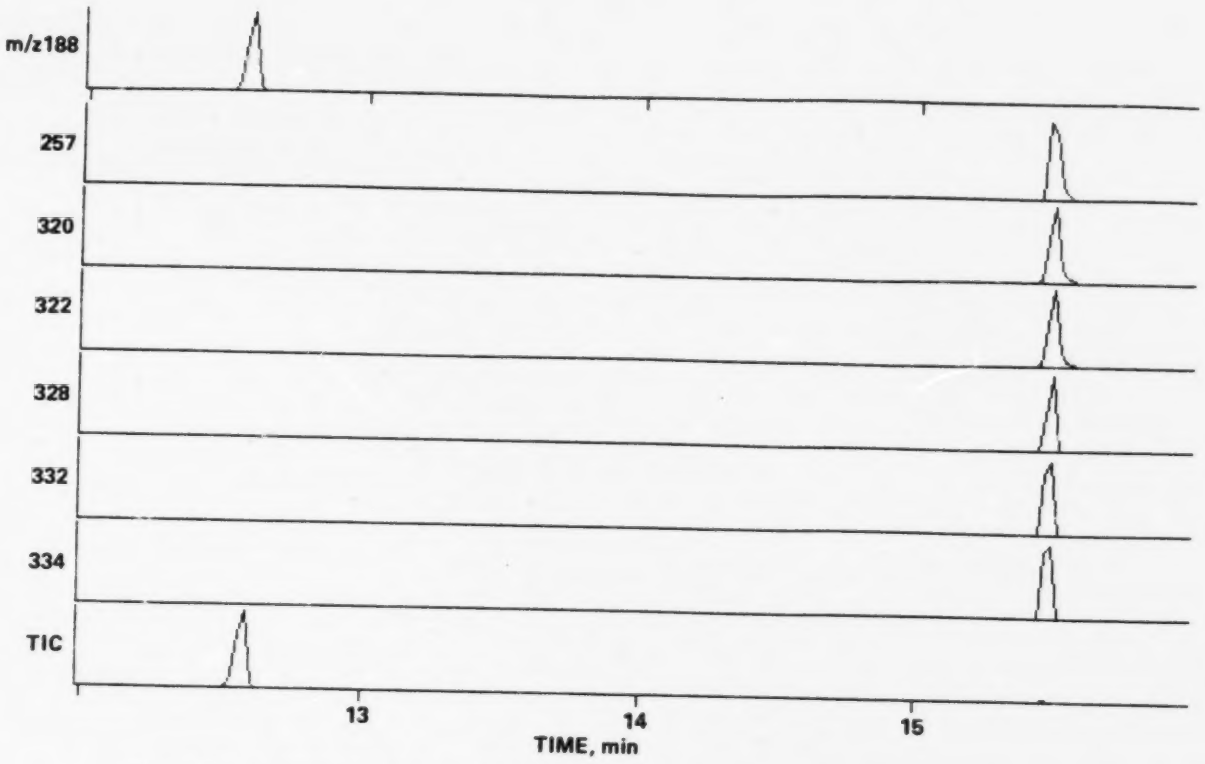

Figure 7A. Partial-scan mass and ion chromatogram of 2, 3, 7, 8-TCDD using the SE 54 GC-column.

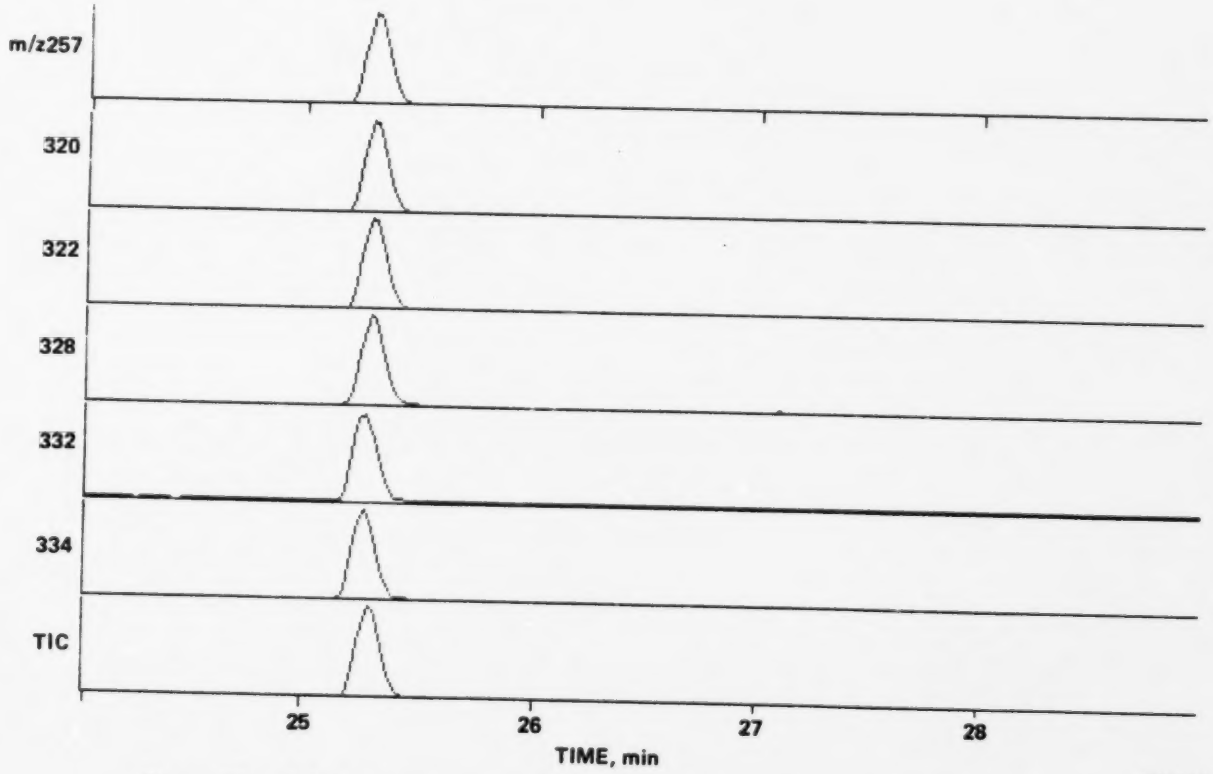

Figure 7B. Selected ion chromatogram of 2, 3, 7, 8-TCDD using the CP-SIL-88 GC-column.

from other interfering TCDD isomers. Figure 8a demonstrates the separation of seven TCDD isomers by using the SE-54 column, and Figure 8b is the separation of the same seven isomers by using the CP-SIL-88 column. Although the SE-54 column provides somewhat faster analysis times, the CP-SIL-88 column yields the isomer specificity necessary to perform the analysis. The detection of 2,3,7,8-TCDD at levels approaching 0.1 ng injected on the GC column (CP-SIL-88) has been estimated for reasonably clean samples. A sample containing 0.03 ng/μL of 2,3,7,8-TCDD would give a signal detectable above background. An extract cleaned up using the EPA Region 7 protocol options A, B, C, or D (15), concentrated to 50 μL, and analyzed by HRGC/LRMS with SIM, would allow a concentration of 0.5 ppm in the hazardous-waste influent sample. The above calculation was based on examples given in Reference 5 and the requirement of 99.99% DRE.

Conclusions

A simple derivatization technique allows the determination of benezene-arsonic acid, hydroxydimethylarsine oxide, and phenylmercuric acetate by the general GC/FID and GC/MS procedures. These compounds can be recovered from materials used in stack sampling quantitatively. The derivatization procedure may be useful for other organometallic compounds. Compounds such as selenourea and tetraethyl lead may be determined by the HPLC/UV and GC/FID or GC/MS procedures, respectively, without major modifications of the procedures. The determination of 2,3,7,8-TCDD by the general procedures provides a screening analysis and would be readily applicable during the survey-analysis portion of hazardous-waste characterization. However, ultimate selectivity and sensitivity are provided by an isomer-specific GC column and selected ion monitoring mass spectrometry.

In future work, we will evaluate methods for other POHCs that are difficult to analyze and apply the methods developed to the analysis of field samples. The determination of organometallics in field samples would aid in validating the method presented in this paper. During the incineration of many hazardous compounds, other compounds not already in the waste could be formed. For example, polychlorinated biphenyls can form polychlorinated dibenzofurans, or organometallic compounds may form inorganic oxides. The identification and development of analytical methods for these products of incomplete combustion (PIC) is underway.

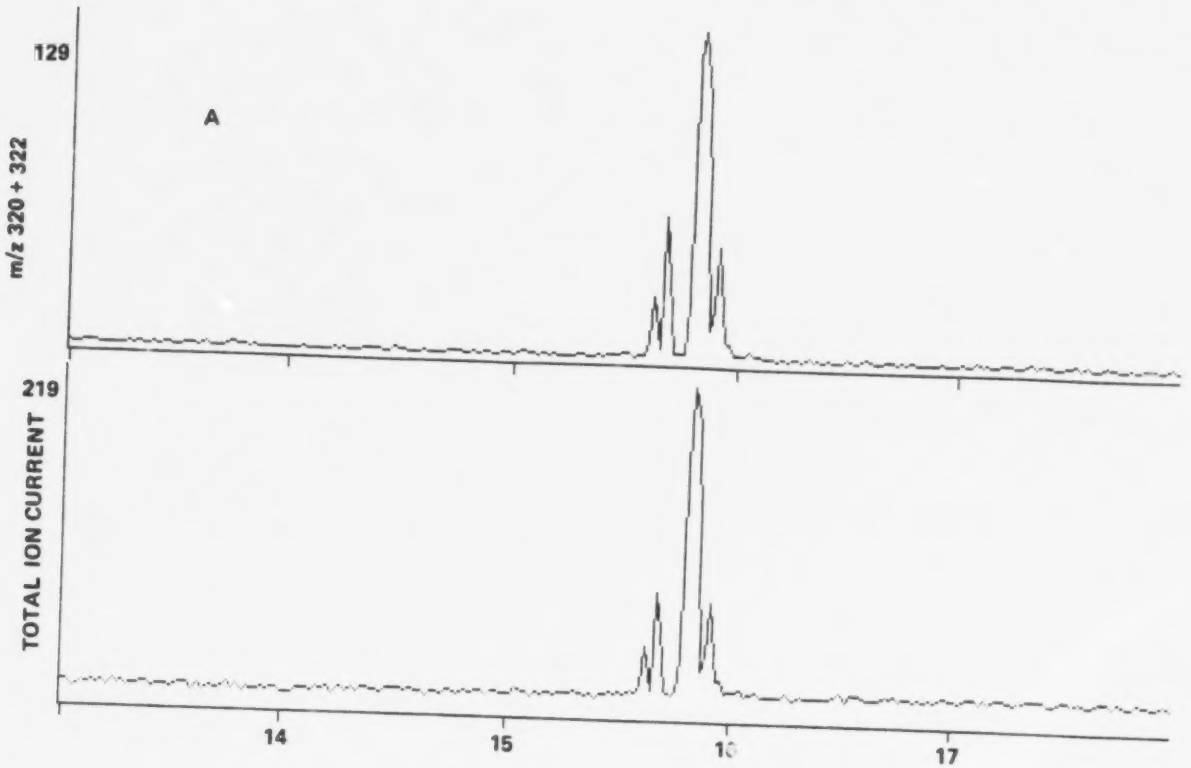

Figure 8A. Separation of seven TCDD isomers with the SE-54 GC-column.

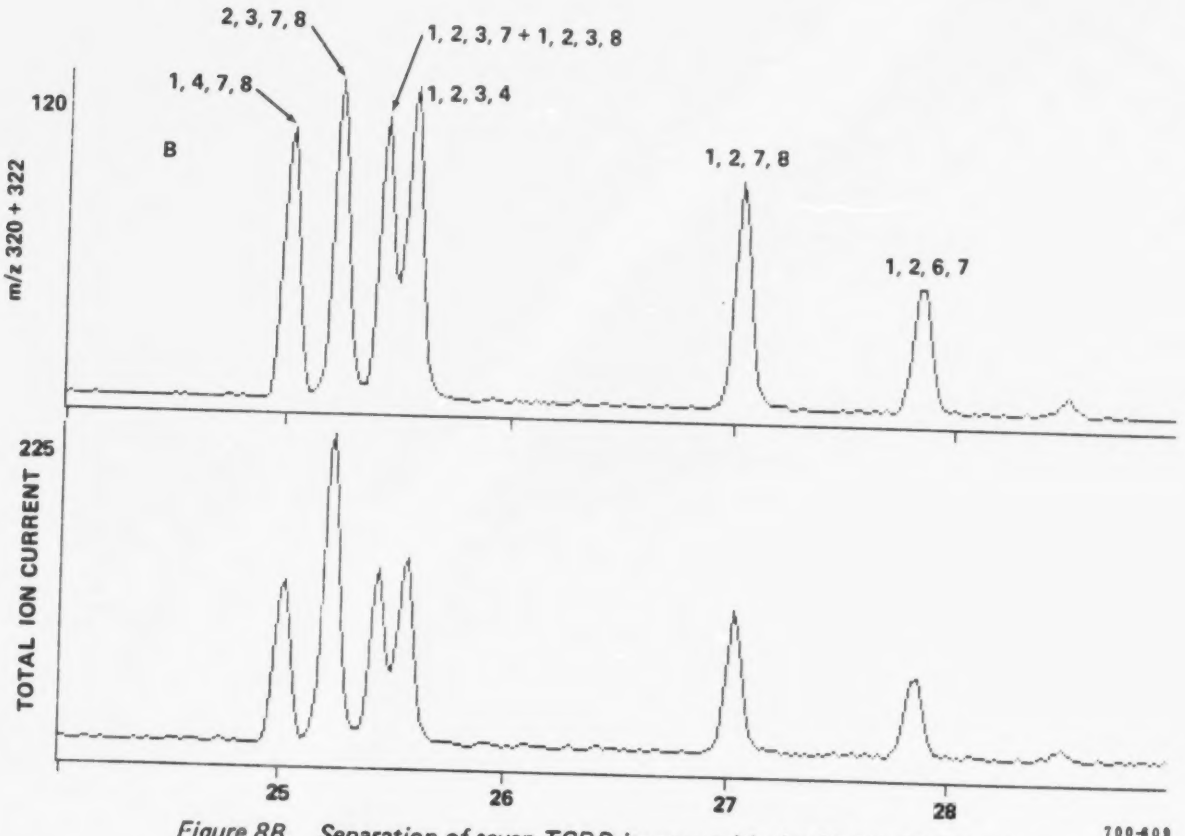

Figure 8B. Separation of seven TCDD isomers with the CP-SIL-88 GC-column.

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